SCH 200
Chemical Bonding

Lecture 5

Chemical Bonding

- What forces hold atoms together to form molecules?
- How do these forces give the molecules particular shapes and qualities?

We can also ponder the following in this section:

- What is a bond?
- How many types of bonds can atoms form?
- Why do atoms form bonds?
- How do atoms bond or how do atoms combine to form molecules?

What is a bond?

- A **bond** may be described as a linkage between a particular pair of atoms e.g. H and Cl in HCl, N and H in NH_3 etc.
- A bond may be described as being strong, weak, long, short, polar or non polar, single, double, triple and even quadruple.

Types of bonds

- The four major types of bonds we shall meet in this study include;
  - *ionic bonds,*
  - *covalent bonds* and
  - *metallic bonds*.
  - *dative* or *coordinate*
- These are in most cases two-centre-two electron bonds.
- A fifth type of bond which is great importance is *hydrogen bond.*

Why atoms combine

- It is a way of attaining chemical stability.
- A molecule (combination of two or more atoms) only forms if it is chemically more stable and has a lower energy than individual atoms.
- The stability is manifested as a lack of reactivity.

Why atoms combine

- **From the electronic point of view**, the most stable electronic arrangement is a noble gas electronic structure and most molecules have this arrangement. Thus, each atom acquires a stable electron configuration by forming one or more bonds.

How atoms combine

- Three theories of bonding
  - Lewis Theory
  - Valence bond theory (VBT) and hybridization of atomic orbitals
  - Molecular Orbital (MO) theory.

Some fundamental ideas in Lewis' theory

- Electrons, especially those of the outermost (valence) electronic shell, play a fundamental role in chemical bonding.
- In some cases electrons are *transferred* from one atom to another. Positive and negative ions are formed and attract each other through electrostatic forces called **ionic bonds**.
- In other cases one or more pairs of electrons are shared between atoms; this *sharing* of electrons is called a **covalent bond**.

Some fundamental ideas in Lewis' theory

- Electrons are transferred, or shared, in such a way that each atom acquires an especially stable electron configuration. Usually this is a noble gas configuration, one with eight outer shell electrons, or an **octet**.

Exceptions

1. In atoms such as Be or B which have less than four outer electrons.

   Even if all the outer electrons are used to form bonds an octet cannot be attained.

Cases where Octet Rule is not obeyed

2. Where atoms have an extra energy level which is close in energy to the *p* level, which may accept electrons and be used in bonding.

   e.g. PF_3 obeys the octet rule but PF_5 does not because the phosphorous uses one 3*s*, three 3*p* and one 3*d* orbitals.

   These violations become increasingly common in elements after the first two periods of eight elements in the periodic table.

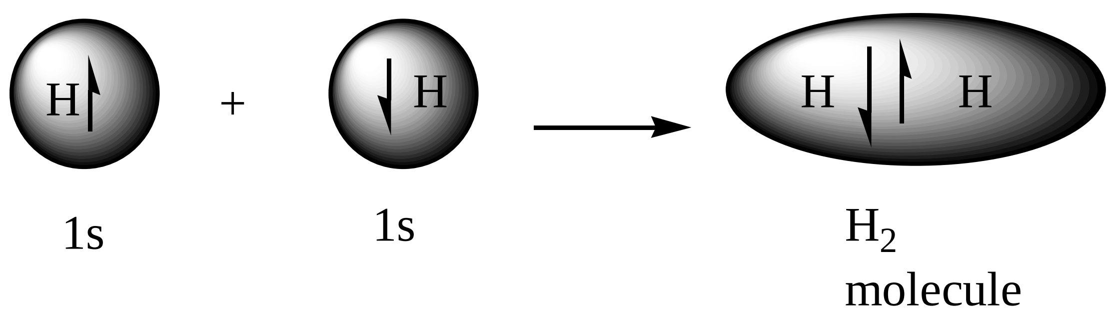
3. The octet rule does not work in molecules with an odd number of electrons such as NO and ClO_2.

Valence Bond Theory (VBT)

- *Also called Localized bond approach*
- Proposed by Heitler and London 1927 and developed further by Linus Pauling and widely between 1940 and 1960.
- It uses three principles to explain bonding:
  - Overlap of atomic orbitals,
  - Hybridization of atomic orbitals and
  - Resonance of molecular structures

Key features of the VBT

1. Covalent bonds are formed by overlap of atomic orbitals, each of which contains 1 electron of opposite spin.



Key features of the VBT

2. For an atom to form covalent bonds it must possess one or more electrons which can pair with those of another atom by canceling their spins.

3. Thus, the number of unpaired electrons determines the valence and paired electrons cannot participate in bonding.

Key features of the VBT

4. Paired electrons can only participate in bonding they can be unpaired with only a small expenditure of energy. This unpairing is generally only possible if it involves no change in the principal quantum number, n. e.g. in C and P
   - C [He]$2s^2 2p^2$ only two bonds are possible
   - C* [He] $2s^1 2p^3$ four bonds are possible
   - Consider P [Ne]$3s^2 3p^3$

Key features of the VBT

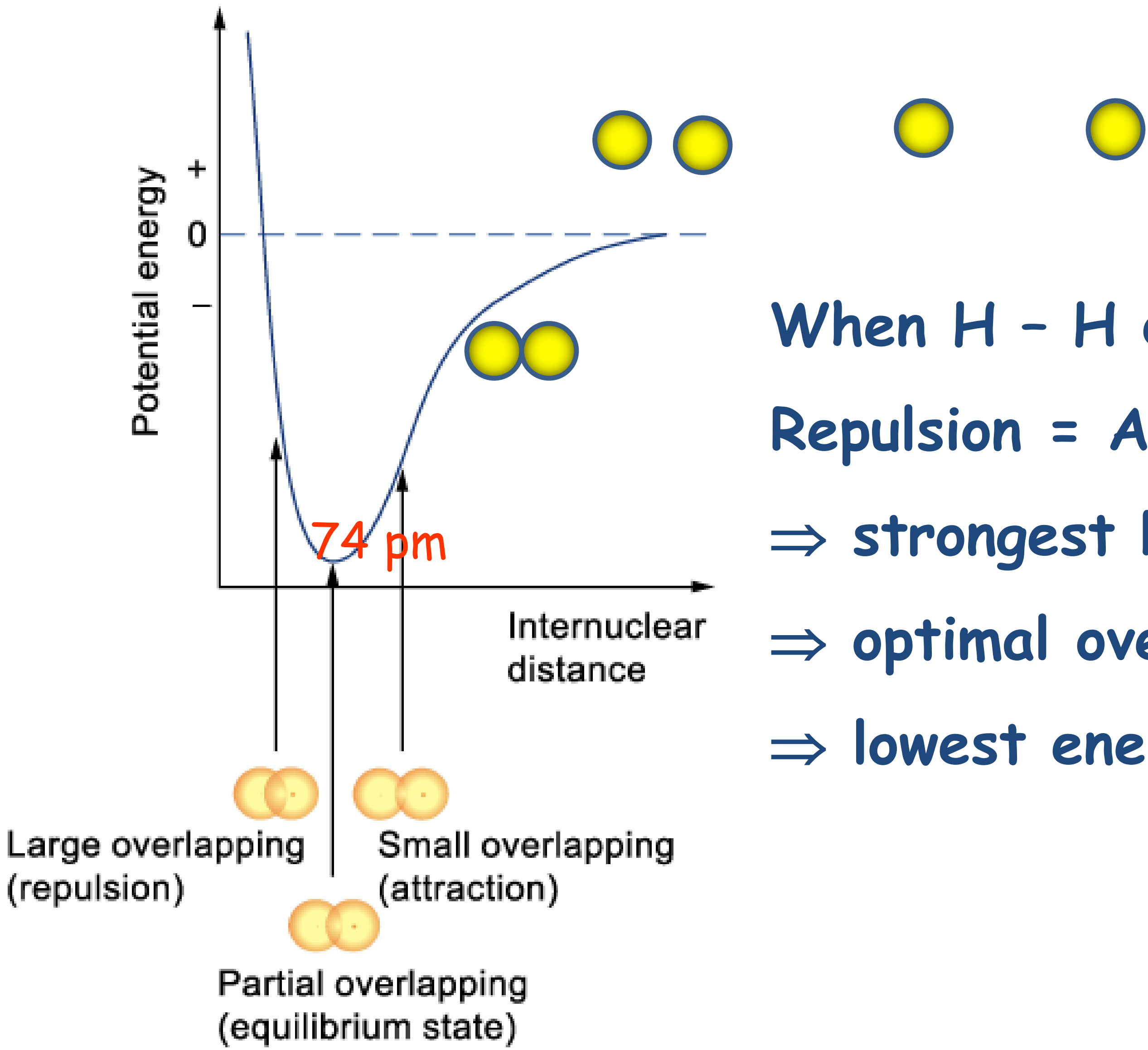
5. Each of the bonded atoms maintains its own atomic orbitals, but the electron pair in the overlapping pair is shared by both atoms.
   – The greater the amount of orbital overlap the stronger the bond.
   – The degree of overlap also varies with type of orbitals. *s* orbitals are same all round while *p* and *d* orbitals overlap best at the tips of the lobes making the bonds directional.

Overlap of Atomic Orbitals

The sharing of electrons between atoms is viewed as an overlap of atomic orbitals of the bonding atoms.

What happens to the energies of the atoms as they approach each other to form a bond?

The overlap of orbitals-Energy well



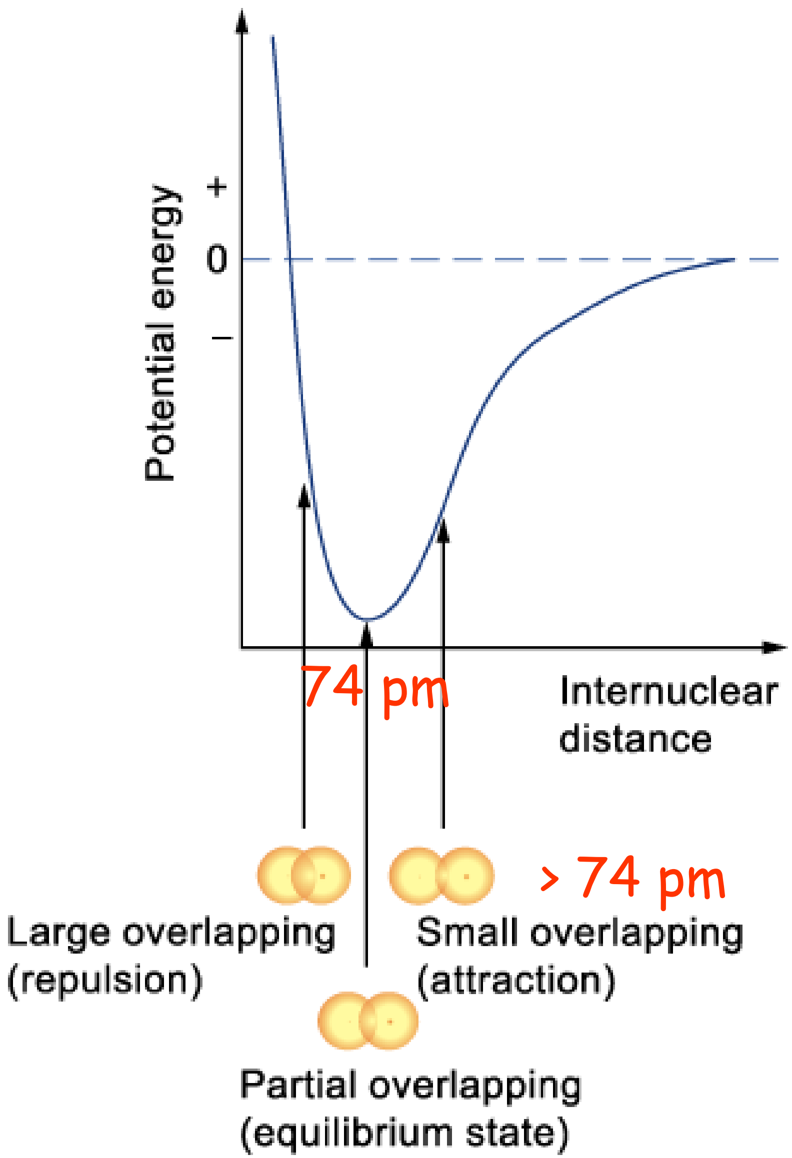
When H – H distance = 74 pm,

Repulsion = Attraction

⇒ strongest bond

⇒ optimal overlap

⇒ lowest energy



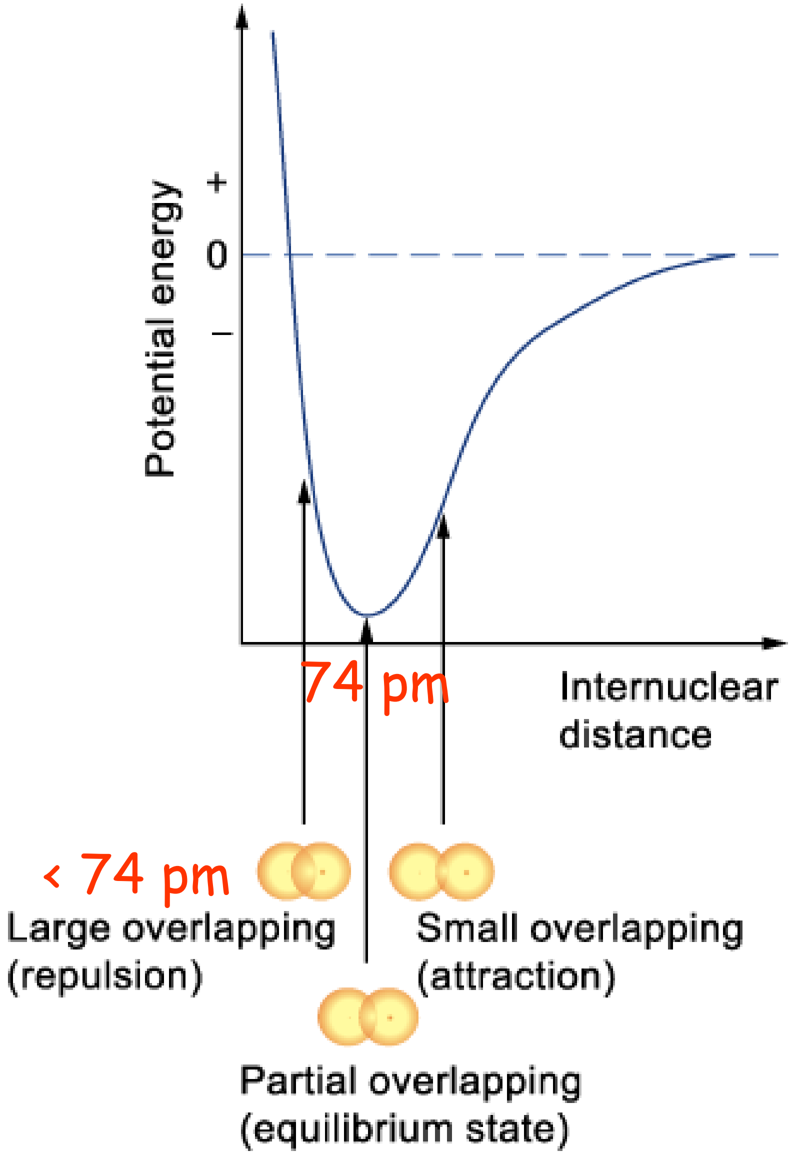
At H – H distance > 74 pm,

Repulsion < Attraction

⇒ weaker bond

⇒ too little overlap

⇒ atoms come closer



At H – H distance < 74 pm,

Repulsion > Attraction

$\Rightarrow$ weaker bond

$\Rightarrow$ too much overlap

$\Rightarrow$ atoms get further apart

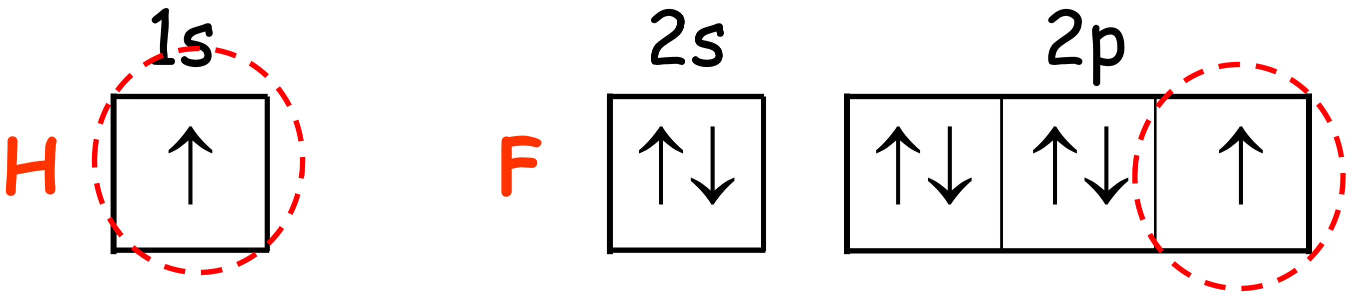
Because of orbital overlap, the bonding electrons localize in the region between the bonding nuclei such that

There is a high probability of finding the electrons in the region between the bonding nuclei.

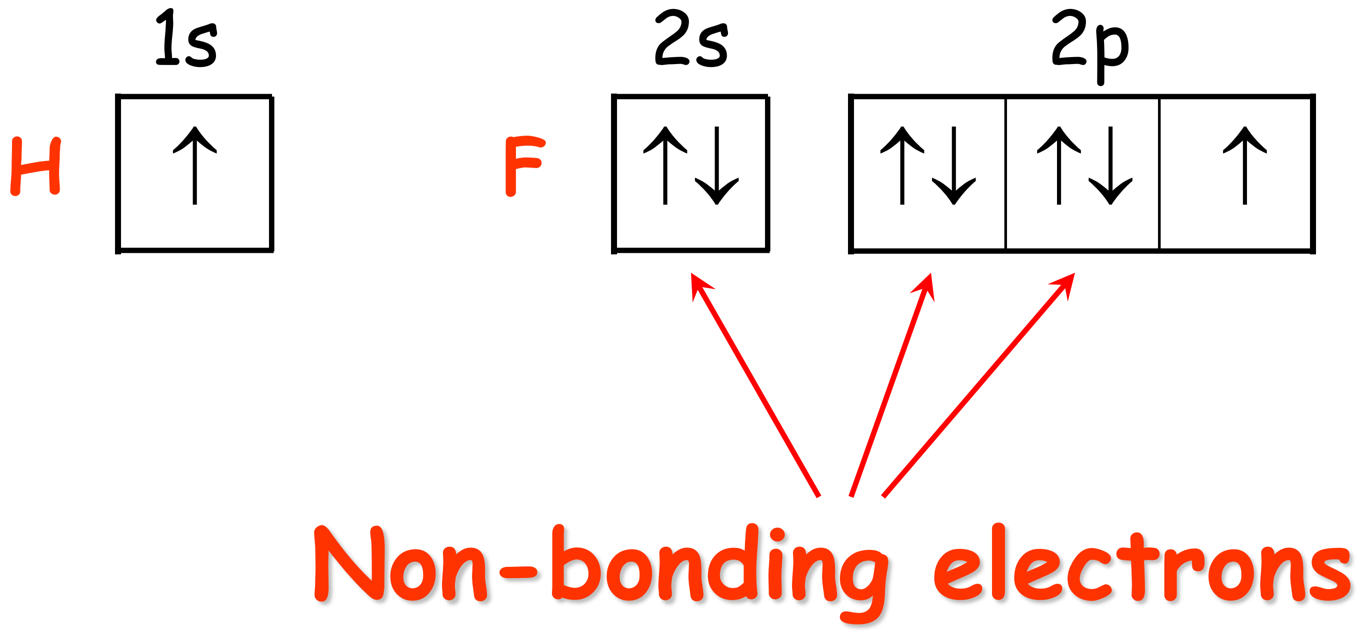
Overlap of two **half-filled** orbitals leads to the formation of a covalent bond.

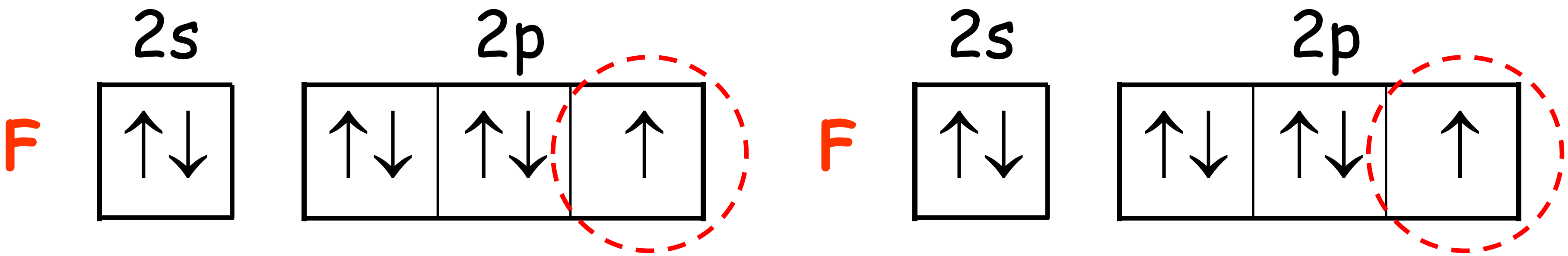
1s 1s

1s-1s overlap gives a H - H single bond

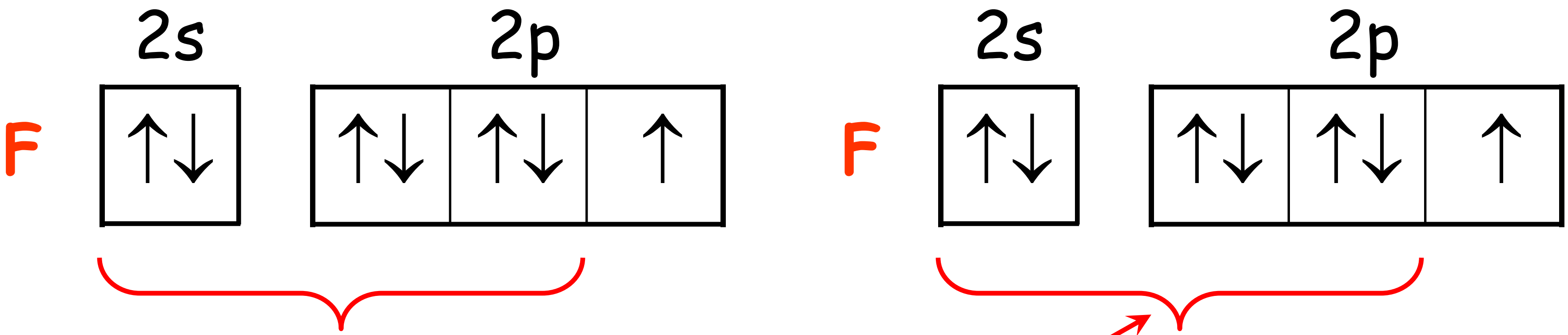


The 1s-2p overlap gives a H – F single bond


1s
2s
2p
H
F
Non-bonding electrons

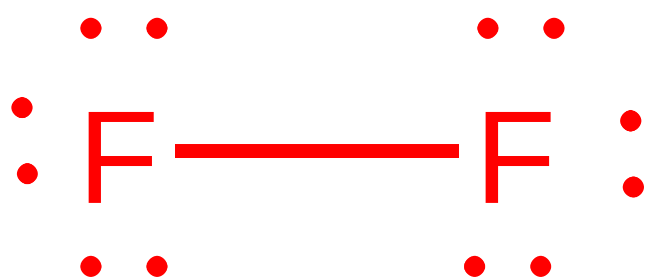


The 2p-2p overlap gives a F - F single bond

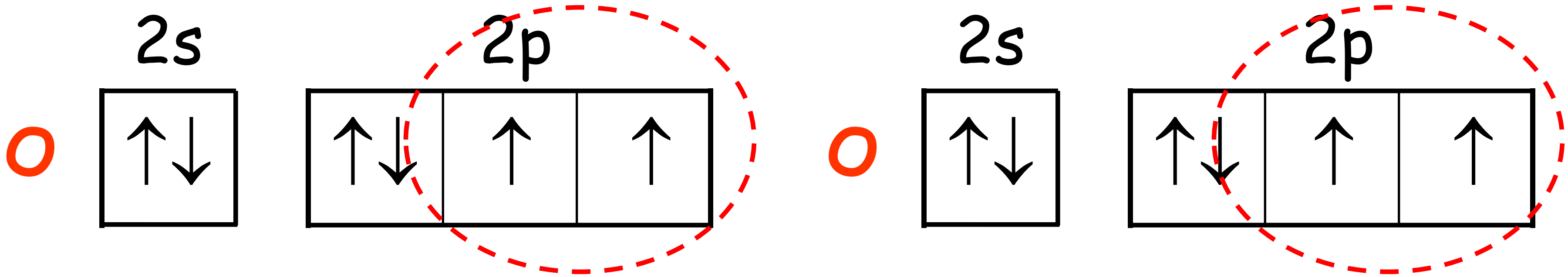


Non-bonding electrons

Each F atom has three pairs of non-bonding electrons.

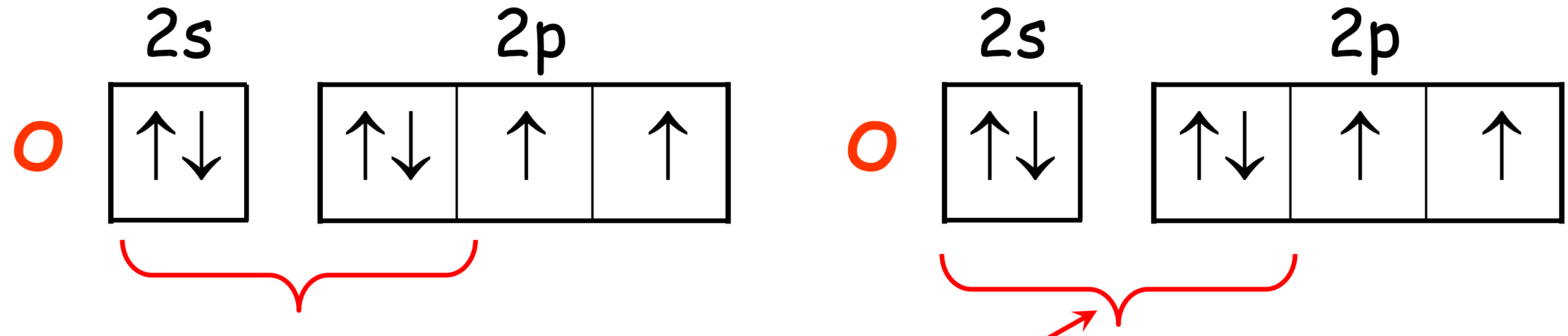


Q Identify the non-bonding electrons in O_2 molecules.



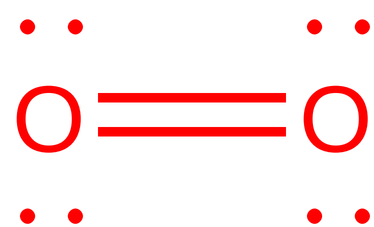
Two 2p-2p overlaps give a O=O double bond

Q.23 Identify the non-bonding electrons in O_2 molecules.



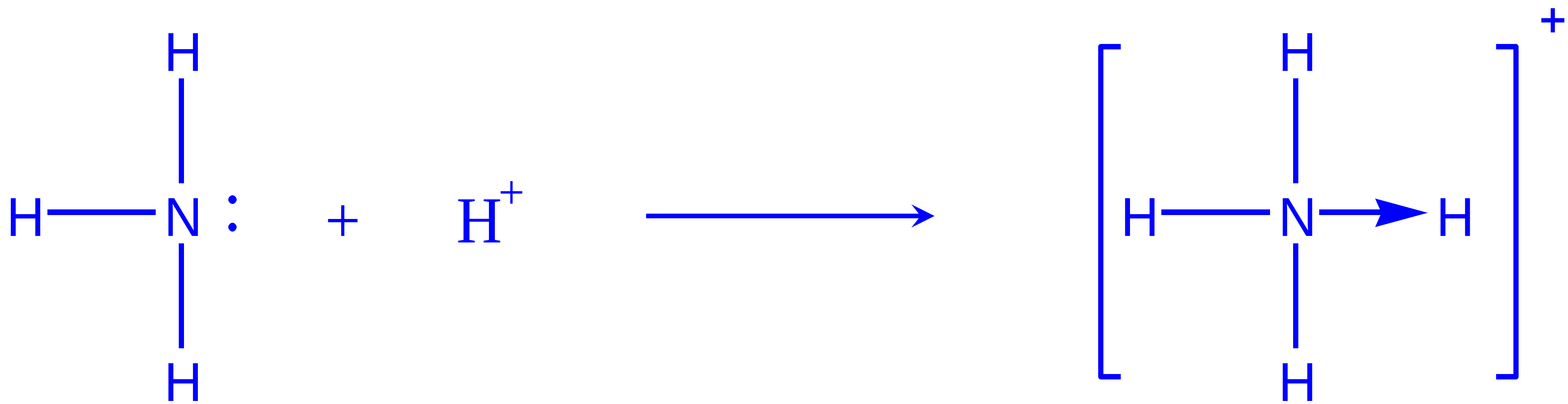
Non-bonding electrons

Each O atom has two pairs of non-bonding electrons.

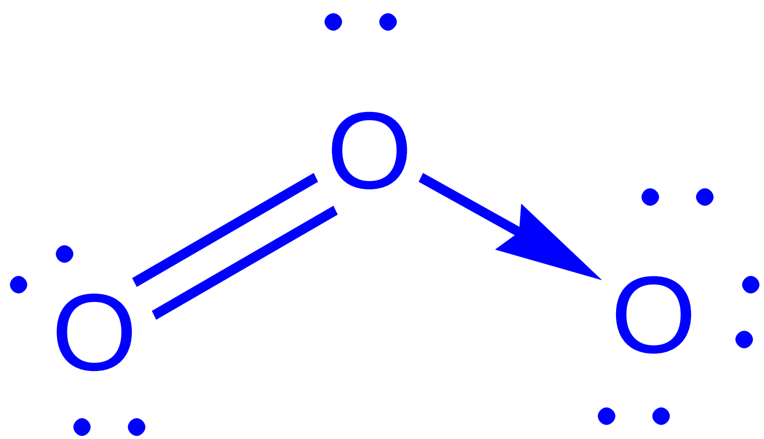


Coordinate covalent bond

Overlap of an **empty orbital** with a **fully-filled orbital** leads to the formation of a **co-ordinate covalent bond** or **dative bond**

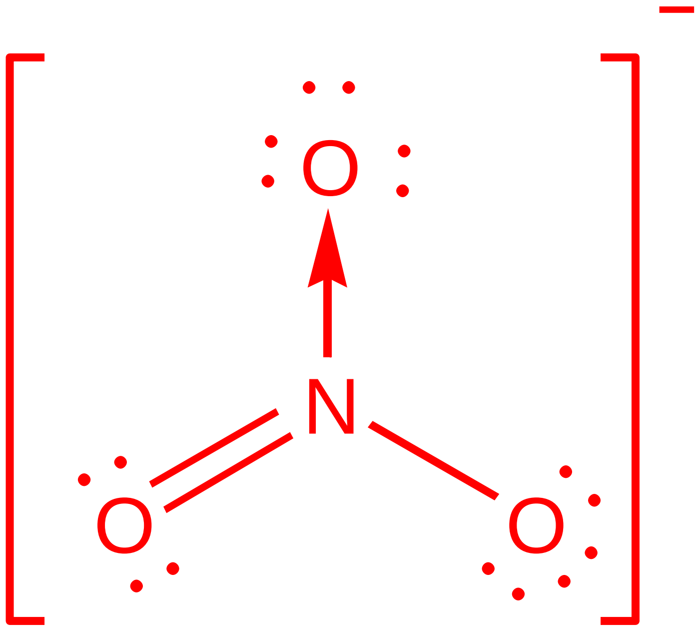


Represented by an arrow → pointing from the electron pair **donor** to the electron pair **acceptor**.



Ozone, O_3

The nitrate anion, NO_3^-



$$F_3B \quad + \quad :NH_3$$

$$\downarrow$$

$$F_3B \longleftarrow NH_3$$

Interpretation of the Formation of Covalent Bonds in terms of Valence Bond Theory

(a) HCN

By Lewis model, the structure is $H-C\equiv N$

$\Rightarrow$ one $H-C$ single bond and

one $C\equiv N$ triple bond.

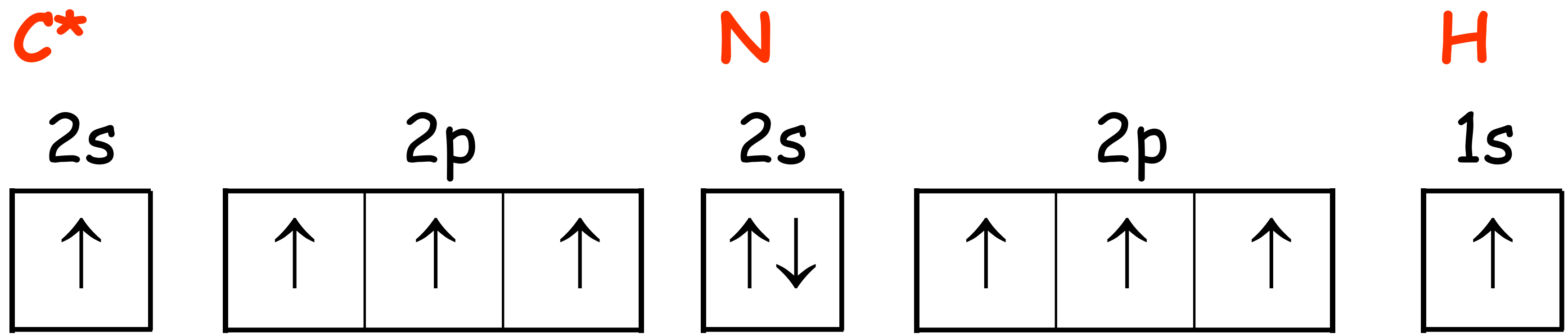
By VB Theory,

	2s	2p		
C	↑↓	↑	↑	

⇒ Only 2 single bonds can be formed.

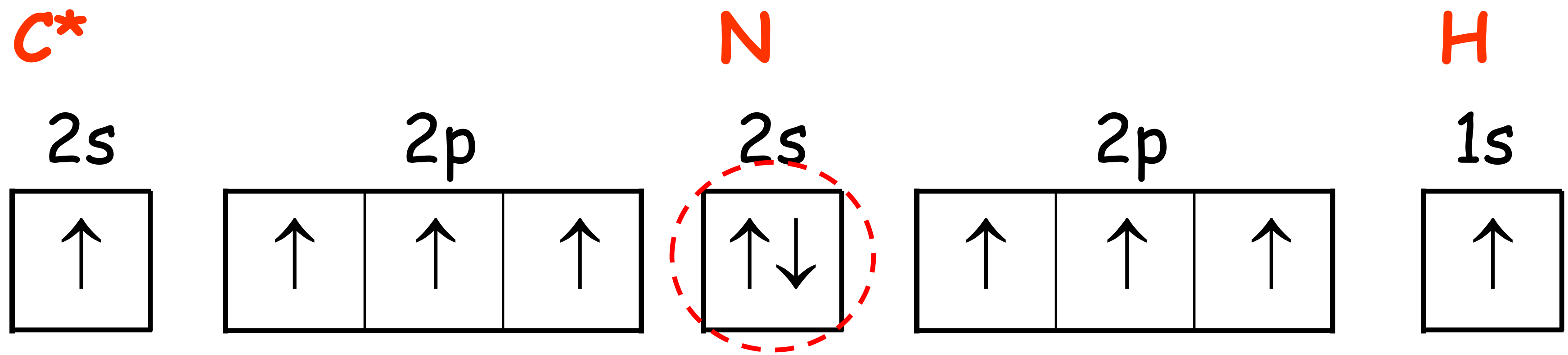
⇒ Promotion of a 2s electron to a 2p orbital.

	2s	2p		
C*	↑	↑	↑	↑

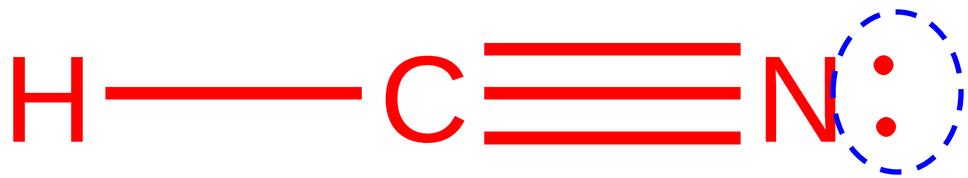


☞ The overlap of one orbital (?) of C* with an 1s orbital of H gives the C-H single bond.

☞ Overlaps of three orbitals (???) of C* with three 2p orbitals of N give the C≡N triple bond.



☞ The 2s electrons on N are non-bonding electrons.



☞ The energy released by forming a stronger triple bond outweighs the energy required for promoting an electron from a 2s orbital to a 2p orbital.

(b) SO_2

By Lewis model, the three possible structures are

$$O \leftarrow S = O, \quad O = S \rightarrow O, \quad O = S = O$$

Most stable $\because$ no separation of charge.

By VB Theory,

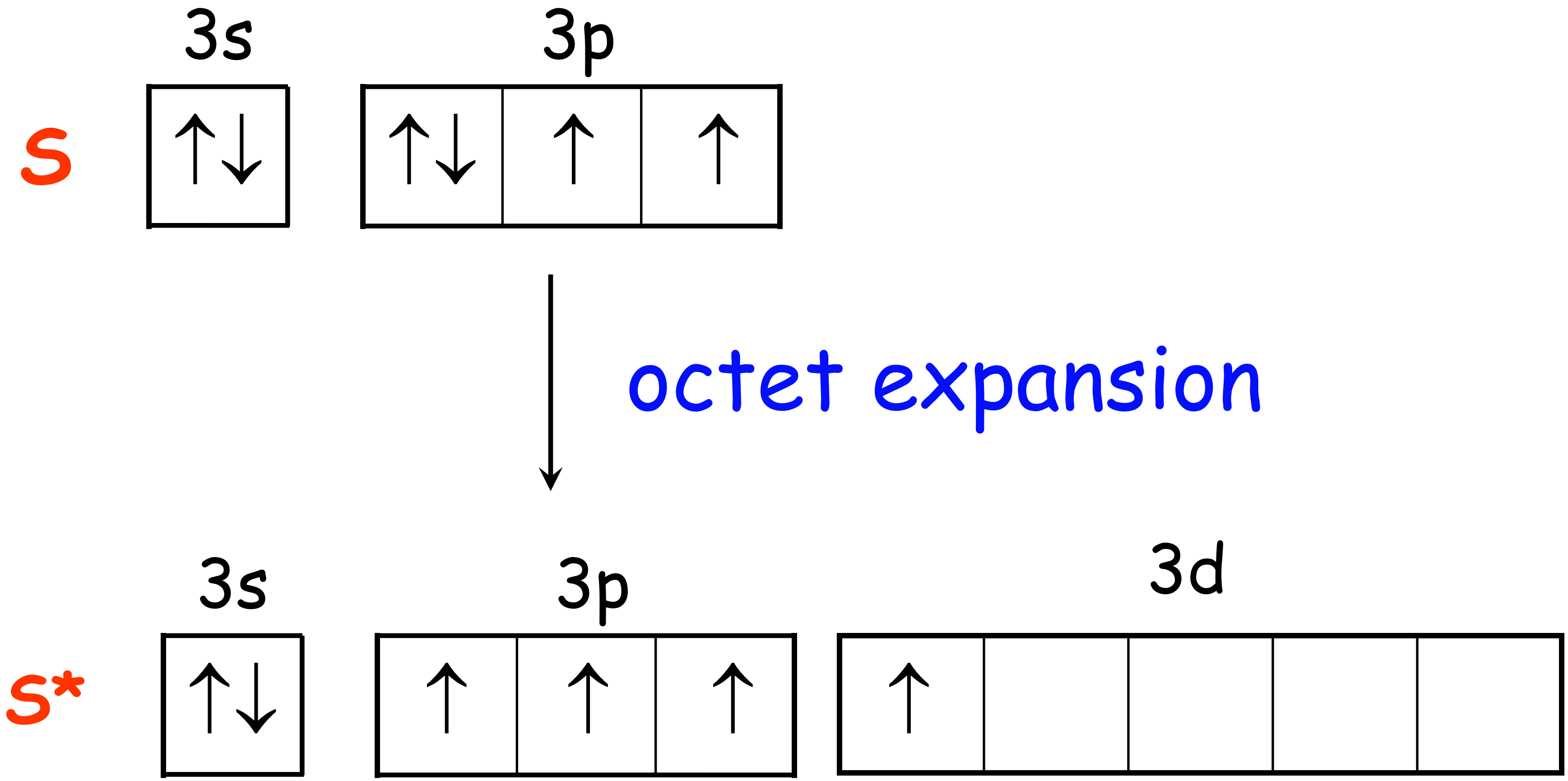
	3s	3p		
S	↑↓	↑↓	↑	↑

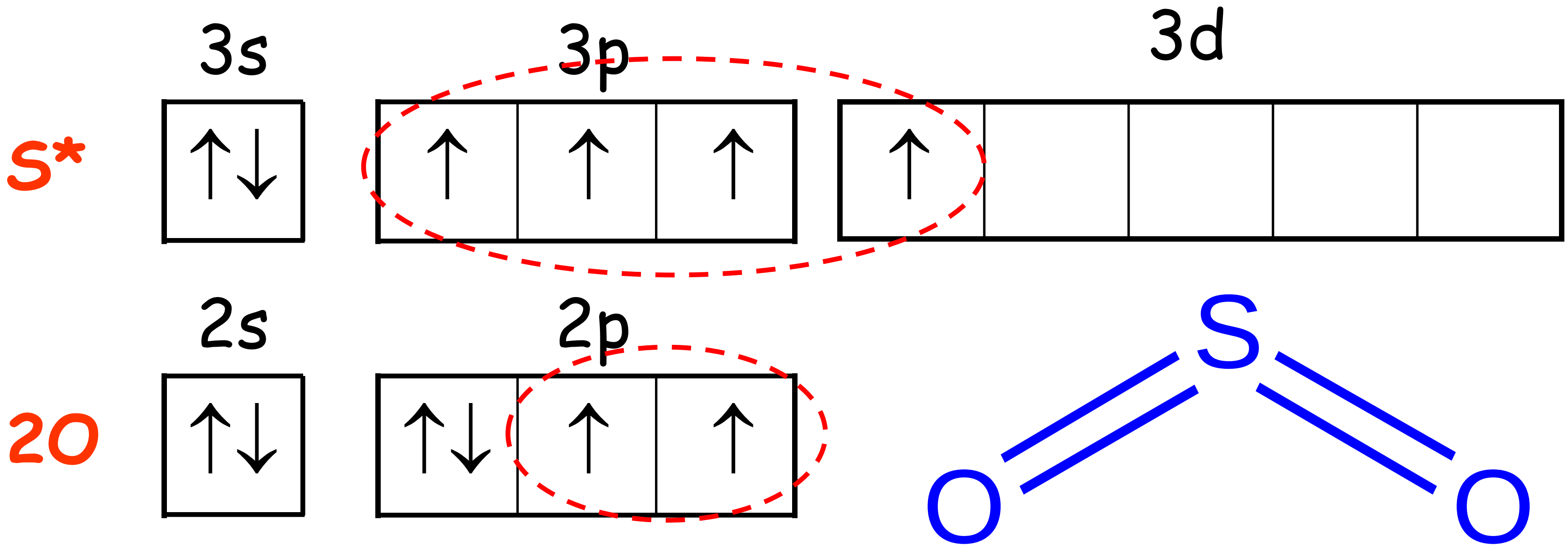
⇒ Only two single bonds can be formed.

⇒ One 3p electron has to be promoted to a 3d orbital.

⇒ Expansion of Octet.

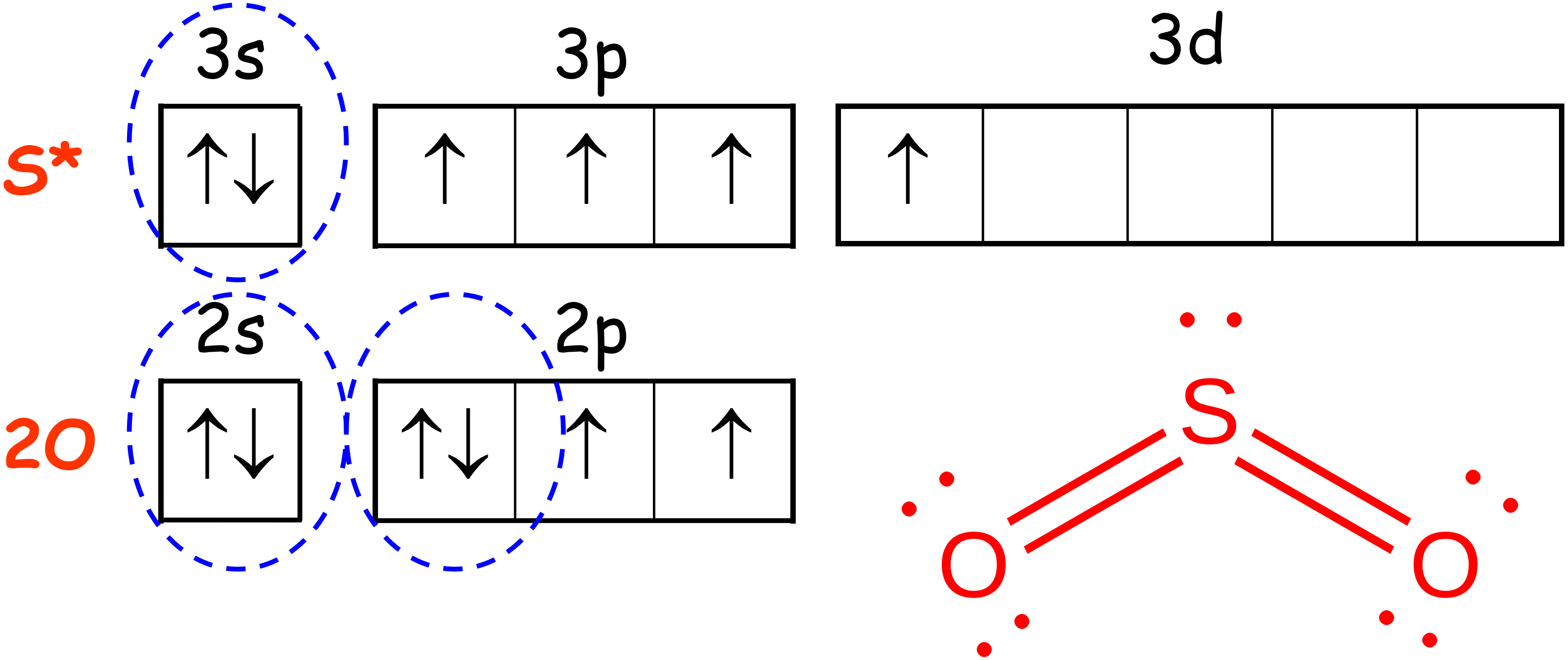
By VB Theory,





☞ **Overlaps of two half-filled orbitals (??) of S* with two half-filled 2p orbitals of an oxygen atom give a S=O double bond.**

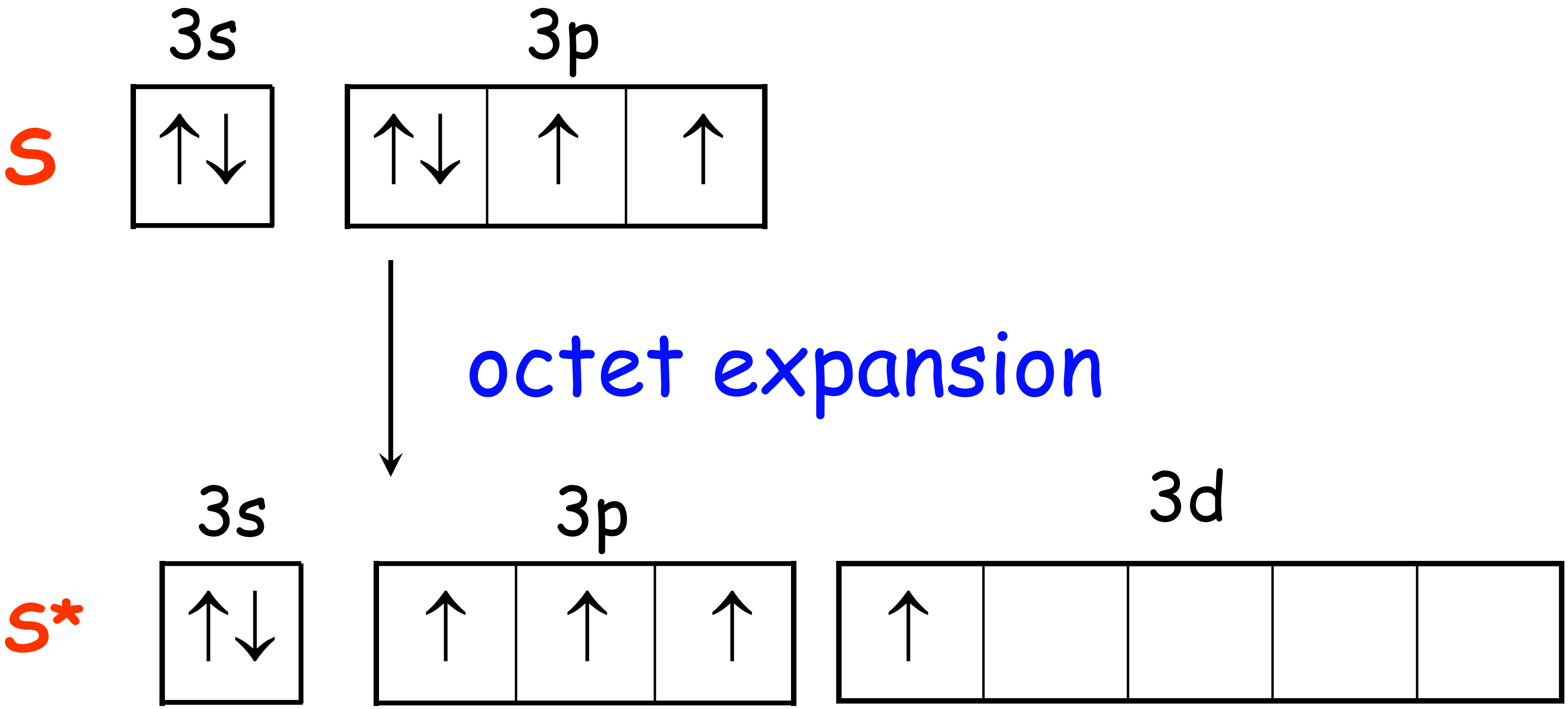
A total of two S=O bonds are formed with two O atoms



Non-bonding electrons :

S* $3s^2$;

O $2s^2$ and $2p^2$



The energy released by forming of two stronger double bonds outweighs the energy required for promoting an electron from a 3p orbital to a 3d orbital.

The Concept of Resonance

According to VB theory, the two less stable structures of SO_2,

$O \leftarrow S = O$ and $O = S \rightarrow O$ do <u>**'exist'**</u>.

Each of these structures contributes to a certain extent to the real structure of SO_2.

If ψ_{SO_2} represents the wave function of the real structure of SO_2 molecules, then

$$\psi_{SO_2} = a\psi_{O=S=O} + b\psi_{O\leftarrow S=O} + c\psi_{O=S\rightarrow O}$$

where $\psi_{O=S=O}$ $\psi_{O\leftarrow S=O}$ $\psi_{O=S\rightarrow O}$

are the wave functions of the three possible structures and

$$a > b = c > 0$$

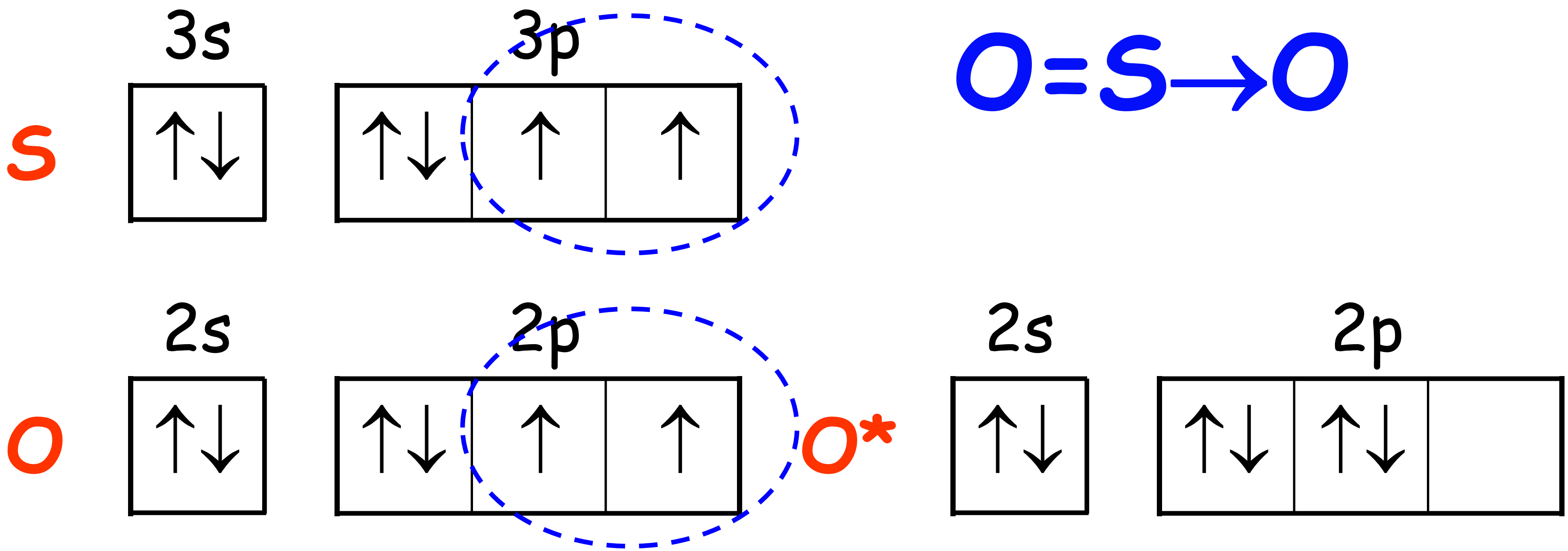
In other words, the real structure of SO_2 is the <u>resonance hydrid</u> of the three possible structures.

$$O{=}S{=}O \quad \leftrightarrow \quad O{\leftarrow}S{=}O \quad \leftrightarrow \quad O{=}S{\rightarrow}O$$

More contribution

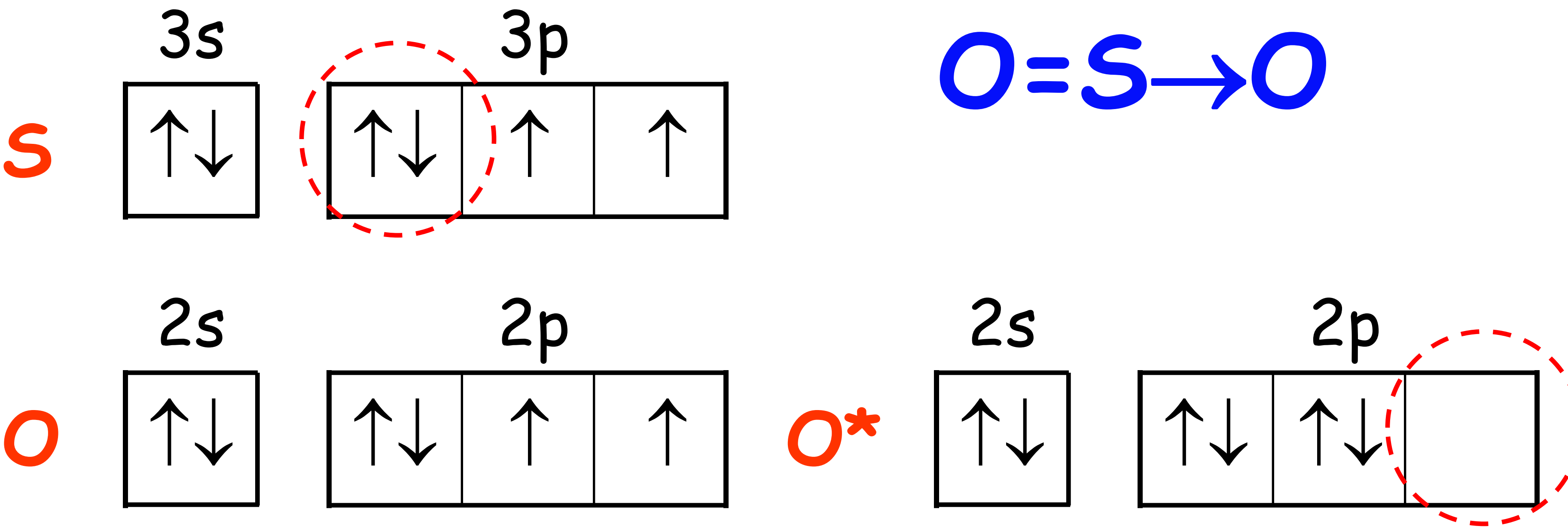
Less contribution

$O{=}S{\rightarrow}O$



A S=O double bond is formed by **3p(half-filled)-2p(half-filled)** overlaps between S and O.

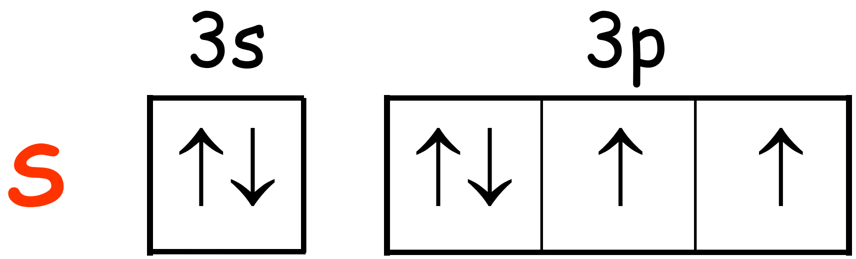
Q.24



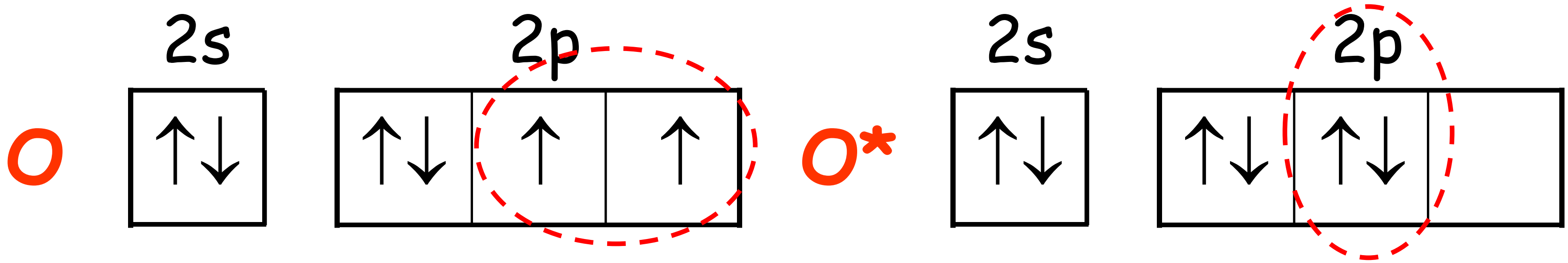
$O{=}S{\rightarrow}O$

A O←S dative bond is formed by 3p(fully-filled)-2p(empty) overlap between S and O*

Q.24

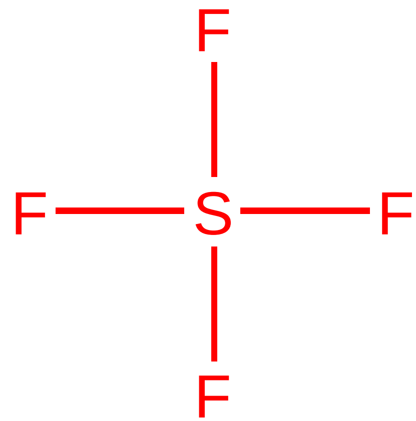
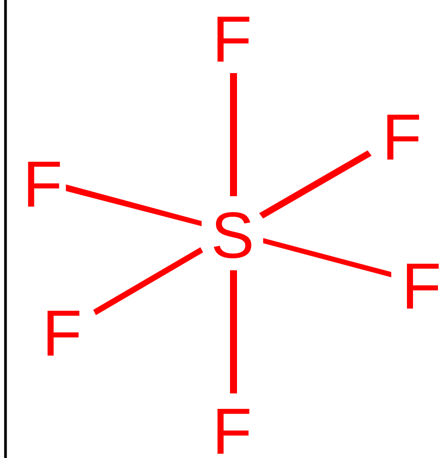


$O{=}S{\rightarrow}O$

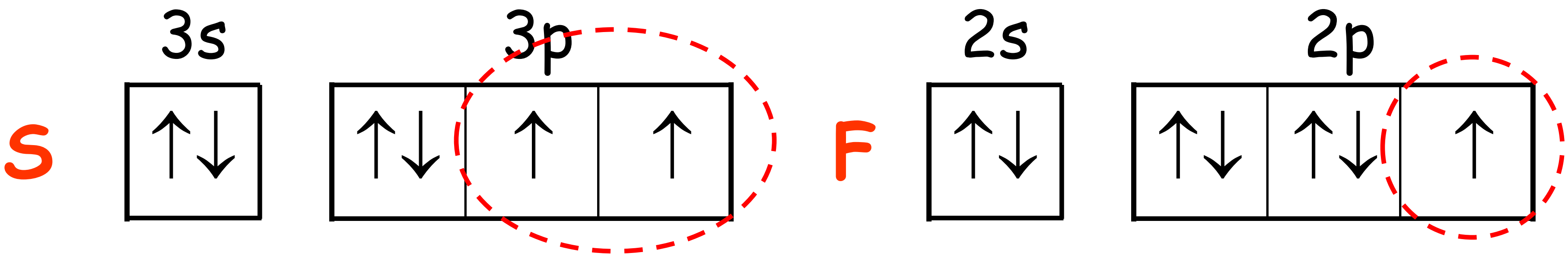


Formation of dative bond is <u>not favourable</u> because the two unpaired 2p electrons in O are forced to pair up to give O*

(c) SF_2, SF_4, SF_6

Molecule	SF_2	SF_4	SF_6
Most stable Lewis Structure	F-S-F		

By VB Theory,

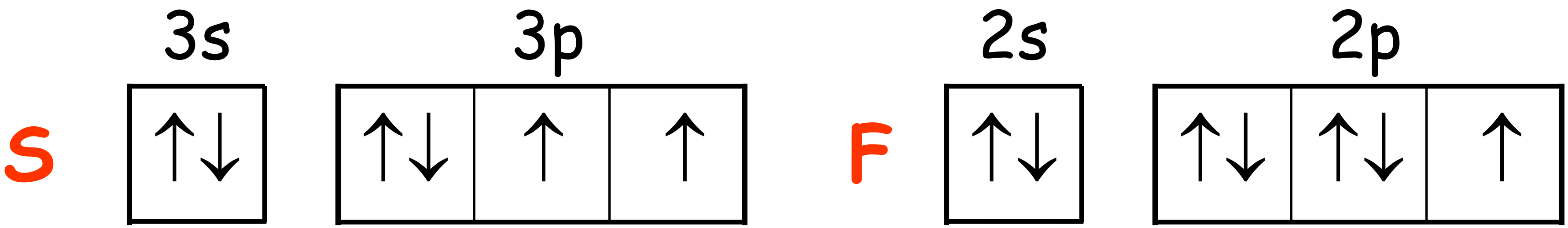


Only two S-F single bonds can be formed by 3p-2p overlaps between one S atom and two F atoms

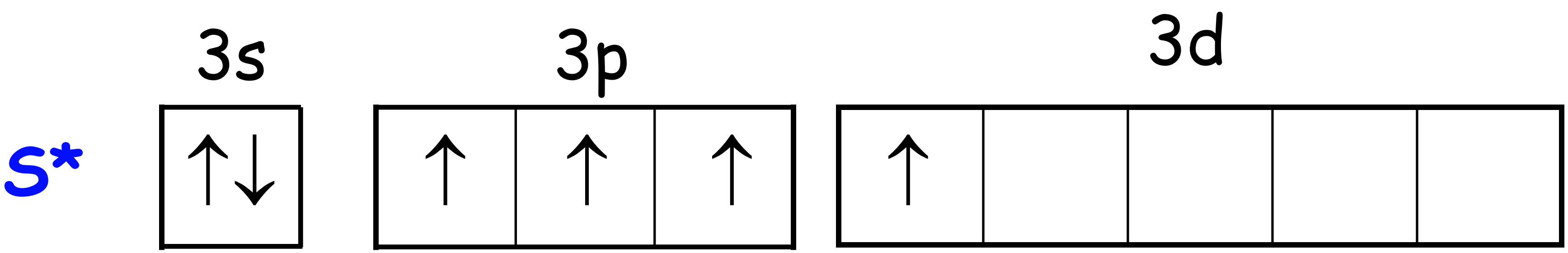
$\Rightarrow$ SF_2 is formed.

F-S-F

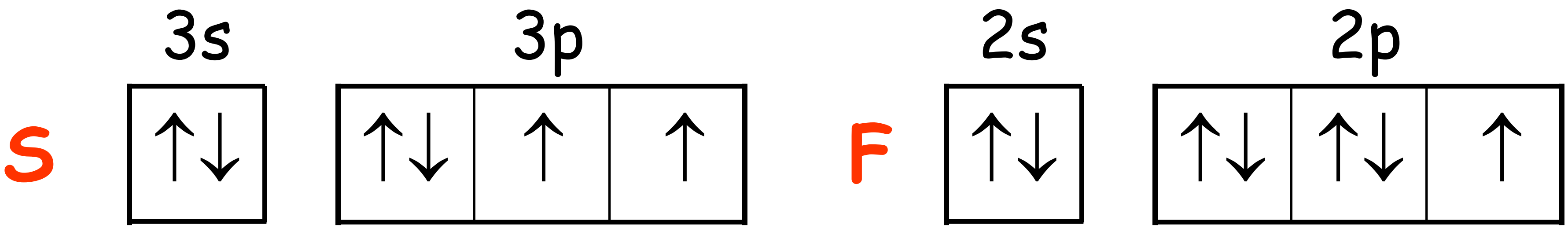
By VB Theory,



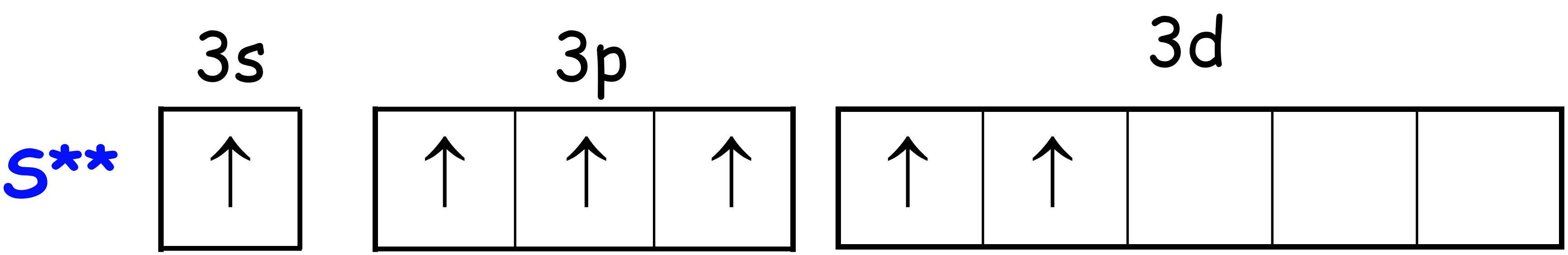
To form four S-F single bonds in SF_4, a 3p electron in S has to be promoted to a 3d orbital.



By VB Theory,



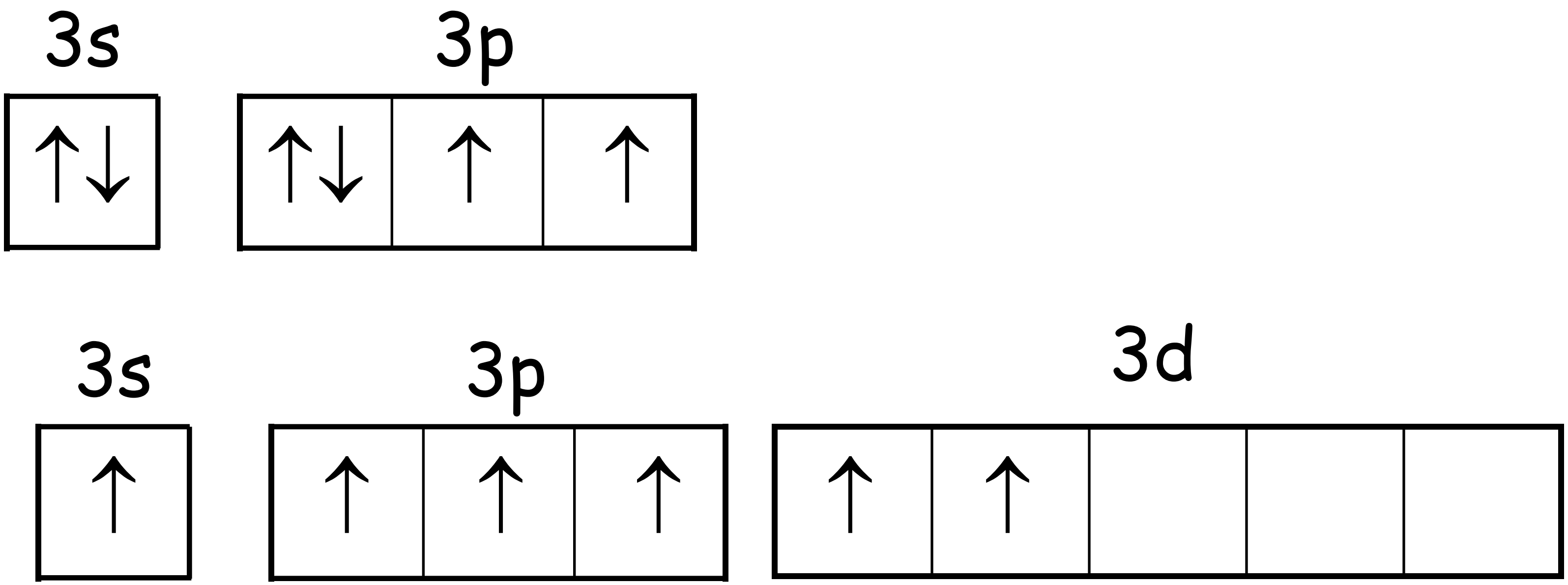
To form six S-F single bonds in SF_6, a 3s electron in S* has to be promoted to a 3d orbital.



By VB Theory,

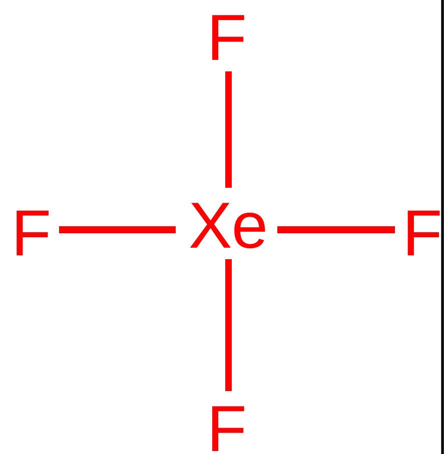
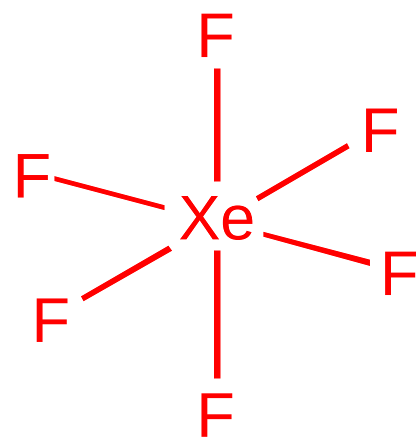
S

S**



The energy released by forming more single bonds **outweighs** the energy required for promoting 3s and 3p electrons to 3d orbitals.

Q.25

Molecule	XeF_2	XeF_4	XeF_6
Most stable Lewis Structure	F-Xe-F		

By VB Theory:

	5s	5p		
Xe	↑↓	↑↓	↑↓	↑↓

	2s	2p		
F	↑↓	↑↓	↑↓	↑

To form two Xe-F bonds in XeF_2, a 5p electron in Xe has to be promoted to a 5d orbital.

	5s	5p			5d				
Xe*	↑↓	↑↓	↑↓	↑	↑				

By VB Theory:

	5s	5p			5d				
Xe*	↑↓	↑↓	↑↓	↑	↑				

To form four Xe-F bonds in XeF_4, a 5p electron in Xe* has to be promoted to a 5d orbital.

	5s	5p			5d				
Xe**	↑↓	↑↓	↑	↑	↑	↑			

By VB Theory:

	5s	5p			5d				
Xe**	↑↓	↑↓	↑	↑	↑	↑			

To form six Xe-F bonds in XeF_6, a 5p electron in Xe** has to be promoted to a 5d orbital.

	5s	5p			5d				
Xe***	↑↓	↑	↑	↑	↑	↑	↑		

By VB Theory:

	5s	5p			5d				
Xe^{**}	↑↓	↑↓	↑	↑	↑	↑			

	5s	5p			5d				
Xe^{***}	↑↓	↑	↑	↑	↑	↑	↑		

The energy released by forming more single bonds <u>outweighs</u> the energy required for promoting 5p electrons to 5d orbitals.